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<b>(21) International Application Number:</b> PCT/US98/03551 <b>(22) International Filing Date:</b> 24 February 1998 (24.02.98) <b>(30) Priority Data:</b> 08/808,376 28 February 1997 (28.02.97) US <b>(71) Applicant:</b> THE WHITAKER CORPORATION [US/US]; Suite 450, 4550 New Linden Hill Road, Wilmington, DE 19808 (US). <b>(72) Inventors:</b> SHARMA, Sunity, K.; 2659 Alma Street, Palo Alto, CA 94306 (US). BHASIN, Kuldip, K.; Apartment #8, 2778 Tyrella Avenue, Mountain View, CA 94043 (US). NARANG, Subhash, C.; 728 Garland Drive, Palo Alto, CA 94303 (US). <b>(74) Agents:</b> VAN ATTEN, Mary, K. et al.; The Whitaker Corporation, Suite 450, 4550 New Linden Hill Road, Wilmington, DE 19808 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> DIRECT DEPOSITION OF GOLD <b>(57) Abstract</b> <p>A process for forming a layer of gold on a substrate, comprising: preparing a solution of a gold precursor wherein the gold precursor consists of <math>\text{Au}(\text{OH})_p(\text{OOCR}^1)_q(\text{OOCR}^2)_r</math>, wherein <math>\text{R}^1</math> is selected from the group of hydrogen, alkyl, alkenyl, and alkynyl, and <math>\text{R}^2</math> is selected from the group of hydrogen, alkyl from 2 to 10 carbon atoms, alkenyl, or alkynyl, and <math>p + q + r = 3</math>. Applying the solution of the gold precursor to the surface of the substrate. Decomposing the gold precursor by subjecting the gold precursor to heat.</p>		

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### Direct Deposition of Gold

The invention is directed to a process for directly depositing a layer of gold on a substrate.

5 Gold compounds have been used in printing and for depositing conductive gold lines in microelectronic circuits. For example, in U.S. Patent No. 4,933,204, a method is shown for depositing gold features on a substrate. Gold(III) hydroxide is dissolved in acetic  
10 acid to form gold(III) acetate. Gold features were then formed by casting the gold(III) acetate film on a suitable substrate such as silicon, and then traversing the film with a laser in the locations where it is desired to produce the conducting lines. The laser was  
15 operated at a power and speed sufficient to heat the traversed locations to a temperature above about 175°C. The gold(III) acetate was decomposed under the heat from the laser to release a layer of gold on the surface of the substrate and release the acetate.

20 A limitation of this method is that the substrate needs to be heated to 175°C. Further, the flexibility of this system is limited by the solubility of the gold(III) acetate in different solvents for the application to the substrate.

25 U.S. Patent No. 5,021,398 shows the synthesis of several metallo carboxylates such as strontium 2-allylhexanoate and barium 2-allylhexanoate. These dimethacrylate compounds are soluble at ambient conditions in polar organic solvents. Furthermore,  
30 metallo carboxylates wherein two or more of the acids are of different chain lengths, i.e. unsymmetrical metallo carboxylates, are much more soluble in the organic solvents than their symmetrical counterparts.

35 What is needed is a gold complex which will decompose to give a gold film at a much lower temperature. Further, what is needed is a gold

precursor with increased solubility in a solvent suitable for the deposition of a gold layer.

In one aspect, the present invention relates to a process for forming a layer of gold on a substrate, comprising:

preparing a solution of a gold precursor wherein the gold precursor consists of



wherein

$R^1$  is selected from the group of hydrogen, alkyl, alkenyl, alkynyl,

$R^2$  is selected from the group of hydrogen, alkyl from 2 to 10 carbon atoms, alkenyl, alkynyl;

applying the gold precursor to the surface of the substrate;

decomposing the gold precursor by subjecting the gold precursor to heat.

It is an object to provide a non vacuum technique for depositing a gold film.

It is a further object to provide a mild method for depositing a gold film on a substrate.

It is a further object to provide an environmentally benign process releasing only environmentally benign byproducts, such as water and carbon dioxide, as main products of the decomposition of the precursor.

As used herein:

"alkyl" refers to alkyl groups having from 1 to 10 carbon atoms, unless otherwise specified;

"alkenyl" refers to organic groups having 1 to 10 carbon atoms and at least one double bond, the unsaturation can be at any location;

"alkynyl" refers to organic groups having 1 to 10 carbon atoms and at least one triple bond.

It has been discovered that gold(III) carboxylates, and preferably mixed gold(III) carboxylates can be used to form a gold film under very mild conditions. Casting

films of the solution results in a film of gold(III) carboxylates. The gold film precursors that the film is prepared from have the formula:



5 where:

p, q and r are real numbers or fractions,

p + q + r = 3.

The gold precursors are typically formed from gold(III) hydroxide in a manner known in the art. An  
10 example of a method to form metallo carboxylates is shown in U.S. Patent No. 5,021,398, which is herein incorporated by reference. The gold precursors are readily soluble in polar solvents such as ethyl acetate, DMSO, etc. The gold precursors can be applied directly  
15 to a substrate in these solvents for the formation of the gold film.

The gold precursors are formed in situ, within the solution which is to be applied to the substrate. Therefore, the exact ratio of the substituents is not  
20 determined. The compounds can be used directly without isolating and determining the ratio of the substituents. It is only important that the amount of gold present in the solution is known.

The substrate on to which the gold can be deposited  
25 can be a metallic material which would typically be electroplated. The precursor can also be used on several other types of material that can not be electroplated. These other substrates are plastics, ceramics, glasses, silicon wafers, cellulose, graphite  
30 and paper substrates. Specific applications of this process can be used for placing a gold layer on electrical contacts, multi-chip modules, printed wiring boards and PCMCIA cards. The process presents an alternative to not only electroplating, but also to  
35 vacuum deposition techniques.

The gold film precursor can be applied to the substrate using a variety of different application

techniques. The choice of a particular technique depends on the end use and mode of production. The precursor can be applied using any one, or a combination, of the following techniques: ink-jet printing, screen printing, spray coating, spin coating, puddle coating, dip coating, brush coating, or various other coating techniques.

Surface pretreatment of the substrate is not absolutely necessary before applying the precursor, however, the gold film adhesion to the substrate may be better if the surface is first activated by removal of grit, dust, grease and other contaminants, prior to application of the precursor solution.

In order to improve the film forming properties of the solution, a small amount of a non-ionic surfactant may be added to the solution of the gold precursor. For example, TRITON X 100 (commercially available from Fluka Chemie AG) can be added to the solution of the precursor. Only a small amount surfactant is added to the solution. For example, less than 0.1% by weight of the surfactant would be added to the solution of the gold precursor. There are many other commercially available surfactants that can be used in the process. During pyrolysis of the gold precursor, the surfactant will decompose. Alternatively, the surface of the substrate, following pyrolysis, can be washed with an organic solvent to remove any remaining organics or surfactants.

Furthermore, the surface of the substrate to be coated with the gold precursor can be first treated with the non-ionic surfactant to allow better adhesion of the gold layer to the substrate. As an alternative, the surface of the substrate to be coated with the gold precursor solution may be pretreated with a reducing agent, such as formic acid or vitamin C.

The precursor solution can be converted to a gold film by heating it to a temperature above about 80°C, and

in some cases, to above about 100°C. This can be accomplished by exposing the solution, in air, to a hot air gun, a laser, or a heat lamp. The temperature that is required to decompose the gold precursor depends on the individual precursor. For example, acetato isobutyrate gold(III) hydroxide will decompose slowly at 80°C to form a gold layer. However, at 100°C, the decomposition will be very fast. Other gold carboxylates will decompose at higher or lower temperatures, depending on the substituents on the gold. For example, thermal analysis of  $\text{Au}(\text{OH})_p(\text{OOCCH}_3)_q(\text{OOCCH}(\text{CH}_3)_2)_r \cdot (\text{H}_2\text{O})_m(\text{CH}_3\text{COOH})_n - ((\text{CH}_3)_2\text{CHCOOH})_o$  shows that the compound mainly decomposes at approximately 75°C and has a second decomposition peak at approximately 100°C.

The choice of a particular gold precursor is dependent upon the substrate to which the gold layer will be applied and how the substrate will stand up under a particular decomposition temperature. Acetato isobutyrate gold(III) hydroxide is particularly well suited for application of a gold layer onto sensitive substrates such as paper or plastic. Other substrates can withstand higher temperatures and therefore a laser could be used to decompose the gold precursor. The length of time needed to decompose the gold precursor will be dependent upon the gold precursor and the power of the laser.

The process herein described could also be used to apply a gold layer to a specific area of the substrate. To accomplish this, the surface of the substrate would be coated with the gold precursor. The laser would then be directed toward particular parts of the substrate in order to decompose the gold precursor on only those parts of the substrate. Once the decomposition of the specific areas of the gold precursor was completed, the surface of the substrate would then be washed to remove

any unreacted gold precursor leaving a gold layer in only those areas that were exposed to the laser.

After a first layer of gold is deposited on the surface of the substrate, it is possible to apply  
5 subsequent layers of gold to the surface by repeating the process. Furthermore, it is possible to apply a thicker coating of the gold precursor to the substrate in order to deposit a thicker layer of gold to the substrate in one step.

10 Examples of methods used to form the gold carboxylates and a gold deposit from the film are given below.

**Example 1**

Preparation of gold(III) hydroxide.

15 Anhydrous gold(III) chloride was prepared by chlorinating chloroauric acid ( $\text{HAuCl}_4$ ) in a slow stream of chlorine gas at 130-140°C. Chloroauric acid in turn was prepared from metallic gold with aqua regia. 2.0 gm of  $\text{AuCl}_3$  was dissolved in 50 ml deionised water to give  
20 a golden yellow solution. To the stirred solution was added basic magnesium carbonate in small portions till no more effervescence occurred. This nearly consumed 4.25 g of basic magnesium carbonate. The solution was stirred for 10 hrs at room temperature. The solution  
25 was filtered and the residue was repeatedly washed with 0.1 N  $\text{H}_2\text{SO}_4$  till no more unreacted carbonate was left. The residue was then washed with water to remove any remaining acid. The residue was then kept in the freezer.

30 **Example 2**

Preparation of acetato isobutyrate gold(III) hydroxide

To 5.0 gm of the hydrated gold(III) hydroxide obtained above was added dropwise to a mixture consisting of 15 ml of acetic acid and 3 ml isobutyric  
35 acids. The reaction mixture was heated at 50 - 55°C for 3-4 hours till near complete dissolution of the gold(III) hydroxide. The solution may still have



brownish turbidity. It was filtered through a microfilter (0.2 $\mu$ m) and a clear golden solution of the precursor was obtained. The solution was concentrated to about 5 ml and a dark brownish-golden solution  
5 resulted which is ready for use to make the metallic gold film. The solution should be protected from light and kept in the freezer.

### Example 3

The solution was applied to the substrate by puddle  
10 coating, that is, the solution was poured onto the substrate and then spread over the surface of the substrate. The substrate was allowed to dry for a couple of seconds to a minute. The substrate was then placed in front of a hot air gun for less than two  
15 minutes to decompose the gold precursor and blow off any organic material produced from the decomposition of the gold precursor.

The gold layer had good electrical conductivity and wear resistance.

20 The preferred embodiments of this invention have been illustrated by the examples described above. Modifications and additional embodiments, however, will undoubtedly be apparent to those skilled in the art. Furthermore, equivalent elements may be substituted for  
25 those illustrated and described herein, and certain features of the invention may be utilized independently of other features. Consequently, the exemplary embodiments should be considered illustrative, rather than inclusive, while the appended claims are more  
30 indicative of the full scope of the invention.

What is Claimed is:

1. A process for forming a layer of gold on a substrate, comprising:  
preparing a solution of a gold precursor wherein  
5 the gold precursor consists of  
$$\text{Au(OH)}_p(\text{OOCR}^1)_q(\text{OOCR}^2)_r$$
  
wherein  
 $R^1$  is selected from the group of hydrogen, alkyl, alkenyl, and alkynyl,  
10  $R^2$  is selected from the group of hydrogen, alkyl from 2 to 10 carbon atoms, alkenyl, or alkynyl,  
 $p + q + r = 3$ ;  
applying the solution of the gold precursor to the surface of the substrate;  
15 decomposing the gold precursor by subjecting the gold precursor to heat.
2. The process of claim 1, wherein  $R^1$  is methyl and  $R^2$  is  $-\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ .
3. The process of claim 2, wherein the gold  
20 precursor is heated to about  $80^\circ\text{C}$ .
4. The process of claim 3, wherein the gold precursor is heated with a hot air gun.
5. The process of claim 1, wherein the gold precursor is heated with a hot air gun.
- 25 6. The process of claim 1, wherein the gold precursor is heated with a laser.
7. The process of claim 1, wherein  $R^1$  is not equal to  $R^2$ .
8. The process of claim 1, wherein the composition  
30 of the substrate is from the group of metal, plastic, glass, paper, silicon wafer, graphite, and cellulose materials.
9. The process of claim 1, wherein a surfactant is added to the solution of the gold precursor prior to  
35 application to the substrate.
10. The process of claim 1, wherein  $R^1$  has at least 2 carbon atoms and  $R^1$  is equal to  $R^2$ .

# INTERNATIONAL SEARCH REPORT

Inte. Jonal Application No

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**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C23C18/08

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 9706 Derwent Publications Ltd., London, GB; Class L03, AN 97-058047 XP002071718 & JP 08 306 645 A (CANON KK) see abstract	
A	DE 39 22 233 A (LINK GUENTER ;MORDIKE BARRY LESLIE (DE); BURCHARDS HANS DIETER (DE) 17 January 1991	

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